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Assessment of Industrial VOC Gas-Scrubber Performance

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Abstract

Gas scrubbers for air-pollution control of volatile organic compounds (VOC) cover a wide range of technologies. In this review, we have attempted to evaluate the single-pass scrubber destruction and removal efficiencies (DREs) for a range of gas-scrubber technologies. We have focused primarily on typical industrial DREs for the various technologies, typical problems, and any DRE-related experiential information available. The very limited literature citations found suggest significant differences between actual versus design performance in some technologies. The potentially significant role of maintenance in maintaining DREs was also investigated for those technologies.

- An in-depth portrayal of the entire gas scrubbing industry is elusive.
- Available literature sources suggest significant differences between actual versus design performance in some technologies.
- Lack of scrubber system maintenance can contribute to even larger variances.
- "Typical" industrial single-pass performance of commonly used VOC gas scrubbers generally ranged from ~80 to 99%.
- Imperfect solid and/or liquid particulates capture (possibly as low as 95% despite design for 99+% capture efficiency) can also lead to VOC releases.
- Changing the VOC composition in the gas stream without modifying scrubber equipment or operating conditions could also lead to significant deterioration in attainable destruction and removal efficiencies.

Introduction

This study was undertaken to gain a better understanding of realistic gas scrubber efficiencies and their effect on the prediction of stack releases from chemical processes. We undertook a literature search for published data from actual industrially operated gas scrubbers in an attempt to understand actual scrubber performance in comparison to stated scrubber design efficiencies. In addition we were interested in the effects of typical operational problems and lack of equipment upkeep on scrubber performance and historical data on the performance of gas scrubbers over a period of time. Due to recent increased industrial interest created by the 1990 Clean Air Act Amendments, this literature search focused more on the removal of volatile organic compounds from industrial gas streams, and generally excluded scrubbing of solid and/or liquid particulates, metals, and high-volume pollutants such as nitrogen and sulfur oxides. Also critical reviews of industrial scrubber performance data were sought while disregarding claims by vendors. Environmental Protection Agency technology evaluation reports not immediately available through University of California resources were excluded.

An extensive literature search using several technical literature databases for the desired industrial data revealed that while municipal waste incinerators burning high-organic content aqueous, liquid and/or solid wastes generally can achieve 99.99% or higher destruction and removal efficiency (DREs), incinerators used in air pollution control (usually referred to as "thermal oxidizers" to avoid confusion with waste incinerators) typically attained significantly lower single-pass destruction and removal efficiencies (~90 - ~99% DRE) with othermore established technologies (e.g., bio-filtration, membrane separation) generally performing with less efficacy (~50–~99% DRE range overall). This document will focus primarily on the expected "design" scrubber performance efficiencies, with some discussion of scenarios leading to degraded scrubber performance, as well as a very brief discussion of efficiencies of solid and/or particulate scrubbers.

Off-gas Scrubber General Discussion

Reviews of general technical literature,[1,2,3] literature journal citations, and vendor sites on the Internet indicate that gas scrubbing is industrially a very broad term that covers solids, liquid, and volatiles/vapor removal from a gas stream. Because the mechanism of separation is similar, solid and/or liquid particulates removal from gas streams use many of the same (although adapted[4]) equipment and are often treated together.[5,6] The gas scrubber technical literature reflects the traditional focus on solid and/or liquid particulate removal from gas streams, although removal of volatiles/vapors from gas vent streams has recently gained importance since the passage of 1990 Clean Air Act Amendments.[7]

Although not a major focus of this document, maximum removal efficiency of solid and/or liquid particles from gas streams depends largely on the particle size. Particle size determines which combinations of seven physical principles are employable for particle removal. As particle size decreases, gravity settling is suitable only for large particles (diameter >40–50 µm); flow-line interception and inertial impaction are efficient down to ~2–3 µm particle diameters; electrostatic forces are somewhat effective below 2–3 µm

[1] Crocker, B.B., Schnelle, Jr., K.B., "Air Pollution Control for Stationary Sources," *Encyclopedia of Environmental Analysis and Remediation*, (R.A. Meyers, ed.), Vol. 1, pp. 150–213, J. Wiley & Sons, Inc., New York, 1998.

[2] Perry, R.H., Green, D.W., Maloney, J.O., editors, *Perry's Chemical Engineer's Handbook*, 7th ed., Sections 14 and 17, McGraw-Hll Co., Inc., New York, 1997 .

[3] Kemmer, F.N., editor, *The Nalco Water Handbook*, 2nd ed., Chapter 41, McGraw-Hill Book Co., New York, 1988.

[4] Fair, J.R., Steinmeyer, D.E., Penney, W.R., Crocker, B.B., "Gas Absorption and Gas-Liquid System Design," *Perry's Chemical Engineer's Handbook*, 7th ed. (Perry, R.H., Green, D.W., Maloney, J.O., ed.), pp. 14–81, McGraw-Hill Co., Inc., New York, 1997.

[5] Kemmer, F.N., op. cit.

[6] Cheremisinoff, N.P., *Handbook of Chemical Processing Equipment*, Chapter 6, Butterworth-Heinemann, Boston, 2000.

[7] Laznow, J., Patkar, A., "Gaseous Toxic Air Pollutant Control Technologies," *Toxic Air Pollution Handbook*, (D.R. Patrick, ed.), pp. 373–97, Van Nostrand Reinhold, New York, 1994.

particle size; diffusional deposition and thermal precipitation are effective for less than ~0.5 µm particle diameter. However, a "collectability gap" exists in the ~0.2–2 µm particle size range.[8] Solid/liquid particle removal equipment include gravity settling chambers, cyclones, centrifugal separators, wet scrubbers such as a spray scrubber or wetted-wall cyclone, plate towers, packed beds, fiber beds, fabric filters, and electrostatic precipitators. When used appropriately, typical single-pass particle collection efficiencies can range from ~60 to ~99% for "typical" dust depending on the equipment used.[9]

Volatiles and vapors in a gas stream can be destroyed or removed by a variety of technologies: thermal oxidation, catalytic oxidation, absorption (regular or with reaction), adsorption, and condensation. Among many factors, volatile/vapor concentration and gas stream flow rate largely determine maximum destruction and removal efficiencies, and hence the methodology selected for remediation of a particular stream.[10] When used appropriately in the air pollution control context, ~50 to ~99% is the typical range for single-pass destruction or removal efficiencies for volatile organic compounds (VOC's) depending on the method employed.[11] Figure 1 shows the typical DREs for the major VOC treatment technologies, and Table 1 illustrates some of the other important factors that can impact efficient VOC scrubbing, as expected by the United States Environmental Protection Agency (USEPA) in 1991.[12] Table 2 lists the typical gas stream flow rates encountered by the different treatment technologies.[13]

VOC scrubbers can be designed to many specific efficiencies, but other factors such as economics (e.g., capital cost, desired use of captured organics), treatment of generated secondary waste streams, and stream pretreatment requirements are also major considerations that may constrain eventual plant efficiencies.[14] For example, an industrial "rule of thumb" for catalytic oxidizers is a catalyst volume sufficient for 90% VOC destruction must be doubled to reach 99% DRE, and tripled to reach 99.9%.[15]

It should be noted that destruction and removal efficiencies cannot be rounded up when reporting capabilities.[16] A calculated 99.988% DRE cannot be rounded up to 99.99% efficiency. Hence, the performance must equal or exceed 99.99%, after rounding to the correct number of significant figures, to be properly claimed capable of 99.99% (or four 9's) efficiency.

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[8] Crocker, et al., op. cit.

[9] Petchonka, J., Hanly, J., "Solid-Gas Separation, Equipment Selection," *Encyclopedia of Chemical Processing and Design* (J.J. McKetta, ed.), Vol. 51, pp. 400–05. Marcel Dekker, Inc., New York, 1995.

[10] Sylvester, R.W., Dyer, J.A., Mulholland, K.L., "Volatile Organic Compounds, Control at Industrial Plants," *Encyclopedia of Environmental Analysis and Remediation*, (R.A. Meyers, ed.), Vol. 8, pp. 5054–68, J. Wiley & Sons, Inc., New York, 1998.

[11] Sylvester, et al., ibid.

[12] EPA Handbook, *Control Technologies for Hazardous Air Pollutants*, EPA/625/6-91/014, Cincinnati, OH, 1991.

[13] Sylvester, et al., op. cit.

[14] Sylvester, et al., op. cit.

[15] Sylvester, et al., ibid.

[16] Gorman, P.G., "Guide for Incinerator Trial Burns," *Standard Handbook of Hazardous Waste Treatment and Disposal* (H.M. Freeman, ed.,), Section 8.15, McGraw-Hill Book Co., New York, 1989.

Gas-Scrubber Technology Review[17]

This study's literature search began attempting to find very equipment-specific industrial performance or efficiency data, historical industrial performance data, industrial equipment degradation or failure information, and comparisons of design and actual performance for a variety of scrubbing equipment (e.g., scrubbers, absorbers, biofilters). The quantitative citations found were usually for mixed or unrelated waste streams. To eliminate a large number of search hits related to fixed gases (mainly carbon, sulfur and nitrogen dioxides) and metals, compound-specific searches focusing on organic amines, alkyl halides, low molecular weight alcohols and organophosphorous compounds narrowed the search to either a lack of or unsuitable literature citations. A broadened focus on volatile organic compounds widened the number and range of citations, but the few potentially suitable citations obtained after sifting through large lists were mostly too general or vague for a quantitative evaluation of actual industrial scrubber performance. The majority of remaining relevant citations were United States government agency reports (e.g., USEPA, National Aeronautical and Space Administration) that were excluded from this study due to lack of immediate availability through the Lawrence Livermore National Laboratory (LLNL) and the University of California, Berkeley and Davis campuses. Limited searching and sifting through the US patents did not yield additional specific or quantitative experiential information.

Hence, a subsequent literature search focusing on the general process of air pollution control related to VOCs was performed to find information regarding actual industrial performance of scrubbers vs. design performance, historical performance of plants since construction, and performance during equipment degradation or failure. Unlike the equipment-specific literature search, general technical literature was found with some industrial anecdotal information. Searches through technical journal publication databases for VOC air pollution control yielded many citations, but again most relevant cited journal articles were too vague or lacked quantitative information. This document is a synthesis of the information obtained from general technical literature (primarily from an article written by industrial consultants) regarding scrubber performance, combined with some very limited inputs from general and technical journal articles.

For each technology, this section covers the basic principle of operation, typical industrial efficiencies, considerations for application of the technology affecting outlet VOC concentrations, typical problems encountered, and in-the-field experiential information, if any (quantitative or otherwise) for each technology. Figure 2 shows process schematics for the methodologies described, and Table 2 lists common secondary environmental impacts for the more common techniques.

<u>Thermal Oxidizers</u>
Thermal oxidizers are a class of VOC control equipment using a combustion device to destroy gaseous air pollutants VOC control specialists prefer this term rather than "incinerator" to avoid confusion with combustion devices used to destroy liquid or solid hazardous waste. Thermal oxidation is a general term that describes techniques such as

[17] Sylvester, et al., op. cit.

flares, regenerative and recuperative thermal oxidizers, catalytic oxidizers, and process heaters and boilers.

Thermal oxidizers usually require air feeds containing VOC concentrations below 25% of the lower flammability limit (LFL), whose maximum VOC feed concentrations (2,500–50,000 ppm for common solvents including hydrocarbons, alcohols, amines, and halogenated compounds[18]) fit well with the acceptable feed concentrations in Figure 1 and Table 1. However some gas streams may have to be diluted with additional air to meet the 25% LFL requirement, and all gas streams will be diluted by the carbon dioxide and water formed in well-designed systems from the combustion of additional fuel to warm the gas stream to the required temperature and maintain the typical 0.3–2.0 second residence time. While capable of accommodating minor flow fluctuations, thermal oxidizers do not handle waste streams of highly fluctuating flow, since increased flow reduces reaction residence time and results in poorer mixing, yielding reduced destruction.[19]

To know the necessary reaction temperature and residence times for the combustion chamber, design of efficient thermal oxidation systems depends on the knowledge of the chemical kinetics of destruction of the specific VOCs of interest. Without small-scale laboratory experiments exhibiting high extents of gas premixing and turbulence providing a good theoretical design basis, design must begin with experience with other chemical species judged to exhibit somewhat similar destruction kinetics. Even with good kinetic information and purposeful attempts to have high gas turbulence, it is frequently found that satisfactory small-scale incinerators yield lower DREs when scaled up to a large-scale incinerator, likely due to poorer gas mixing at the larger scale.[20]

Despite the flexibility of thermal oxidizer systems in handling a wide range of VOCs, different air pollution control systems can be required for different classes of organic compounds. Halocarbons and sulfur-containing compounds often require post-combustion acid-gas scrubbers unlike their hydrocarbon-burning counterparts, and halocarbons require higher combustion temperatures (or alternatively longer residence times[21] above a compound-specific minimum temperature) to avoid formation of products of incomplete combustion (PICs) such as carbon tetrachloride, chlorinated phenols, polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDs), and phosgene.[22] Addition of corrosion-resistant materials to process equipment is often required. Hence a thermal oxidation system that is normally used for just treating hydrocarbons will either have to change operating temperature (and possibly add acid-scrubbing equipment) or face increasing emissions of PICs if halogenated hydrocarbons are added to the waste gas stream.

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[18] "Properties of Common Solvents," *CRC Handbook of Chemistry and Physics* (D.R. Lide, ed.), 72nd ed., pp. 15-43 to 15-50, CRC Press, Boca Raton, FL, 1991.
[19] Laznow, et al., op. cit.
[20] Crocker, et al., op. cit.
[21] Laznow, et al., op. cit.
[22] Chen, B., Cook, R.L., Wright, J.D., "Chlorinated Hydrocarbons, Destruction of," *Encyclopedia of Environmental Analysis and Remediation*, (R.A. Meyers, ed.), Vol. 2, pp. 1056–82, J. Wiley & Sons, Inc., New York, 1998.

As most thermal oxidizer systems are custom-designed, instruction manuals for operation and maintenance usually comprise a series of manuals from the original manufacturers of each system component. Hence the instruction manual may not be as useful as expected from a systems operation perspective, often requiring field modifications to the operating instructions to deal with unanticipated system-related problems.[23] Some general required maintenance pertaining to operational efficiency include burner inspection for signs of corrosion or warpage, burner area cleaning of any accumulated dirt, carbon or foreign matter, inspection for hairline cracks in welds caused by poor thermal design, and seal verification for any shut-off dampers to or from the combustor as well as any related ductwork.[24]

Afterburners are the most simple form of oxidizer, combusting VOC-laden air with supplemental fuel using a pilot, a burner and a stack. Afterburners are usually operated to >99% DREs. Since there is no heat recovery, it is usually used for small (500–3,000 scfm) or intermittent sources. When destroying halocarbons, acid-resistant enhanced materials of construction are required and often a quench and water absorber are used to control acid gas emissions.

Recuperative thermal oxidizers add a heat exchanger at the combustor outlet of an afterburner to preheat the VOC-laden feed gas using the hot combustor discharge gas. Destruction efficiency in the combustor is typically greater than 99%, but gas leakage in the heat exchanger typically reduces destruction efficiency by 0.5–2.0%. When treating halogenated or sulfur-bearing VOCs, the formed acid gas often corrodes the metal heat transfer surface thatcould enhance leakage , usually at the coldest point on the hot side of the heat exchanger.

Regenerative thermal oxidizers (RTOs) have an afterburner -like combustion chamber using a ceramic bed warmed from a previous operation to preheat the VOC-laden feed gas and exhausting the combustion gases through another ceramic bed to recover heat for future operations. This design typically achieves a 97-99% DRE, with reduced destruction attributed to valve leaks and gas bypassing the combustion chamber. Gas flow paths are reversed periodically, which allows some uncombusted VOCs to escape to the stack. In low VOC concentration (<100 ppm) treatment, two RTOs employed in industry (Louisiana Pacific Corp. and 3M Co.) with demonstrated 98-99% operating efficiencies in tests received air emission permits specifying a 95% "design destruction efficiency."[25] Halogenated compounds require special materials of construction and reduce allowable heat recovery to avoid acid condensation.

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[23] Tyler, J.M., "Combustion Systems," *Handbook of Air Pollution Control Engineering and Technology* (Mycock, J.C., McKenna, J.D., Theodore, L., editors), Chapter 11, Lewis Publishers, New York, 1995.
[24] Tyler, ibid.
[25] Zerbonia, R.A., Spivey, J.J., Agarwal, S.K., Damle, A.S., Sanford, C.W., *Survey of Control Technologies for Low Concentration Organic Vapor Gas Streams,* U.S. Environmental Protection Agency, Report #EPA-456/R-95-003, Research Triangle Park, NC, May, 1995.

Air streams containing VOCs are sometimes introduced with combustion air entering process heaters and boilers to recover the fuel value of the waste gas stream, if the air flow rate is small compared to the total combustion air flow rate and VOC concentrations are well below the LFL.

Flares are very much like an open-air afterburner, typically used to treat small (<~200 scfm) fuel-rich streams, due to high fuel costs, that contain little or no oxygen. Some flares are enclosed to reduce local noise, light and heat problems. To obtain the minimum 98% DRE, the gas to be treated must have a heat content of at least 200 BTU/scf or 300 BTU/scf when steam or air-assisted. Flares are regarded as unsuitable for continuous destruction of halocarbons.

Catalytic oxidizers are similar to recuperative thermal oxidizers except that the combustor operates at lower temperatures (typically 315–600°C for hydrocarbons, rather than 760–870°C in non-catalytic systems) and a catalyst bed in the combustion chamber is used to combust the VOCs. Catalytic combustors are typically designed to achieve 90-99% DRE on streams ranging from a few hundred to 500000 scfm, and are not as broadly applicable as regular thermal oxidizers because DREs depend on the nature of the VOC-catalyst interactions. When treating halogenated hydrocarbons, Pt catalysts typically used for hydrocarbons are inhibited by the presence of chlorine, and requires a Pt/Pd bimetallic catalyst to attain 99% DRE.[26] Catalysts are susceptible to damage from overheating due to surges in VOC concentration causing crystal growth or structure change, masking from particulates or dust in the gas stream, and poisons often generated due to the presence of non-hydrocarbons in the system. Dilution of the gas feed stream is required if the heat content exceeds 10 BTU/scf.[27] Poisons can include sulfur, halogens, silicon, zinc, phosphorus, many metals, and some other elements, although halogen-poisoning resistant catalysts have been developed. If packed bed catalysts are used, pelletized catalyst has been found to be superior where large amounts of phosphorus compounds are present.[28] Chemical reactions between the poison and the catalyst active site lead to permanent deactivation, while some poisons merely sorb onto the active catalyst sites.[29] The amount of catalyst required (typically 0.07–0.4 sec residence time) by a particular gas treatment operation is typically selected based on past vendor experience. In practice, most catalytic oxidizers are operated below 99% destruction efficiency since gas by-passing the catalyst bed limits the maximum DRE. If during operation catalyst activity decreases due to deactivation, a common practice is to raise the operating temperature to regain desired destruction efficiency rather than regenerate the catalyst. However, catalytic selectivity may decrease and an increased rate of catalyst aging/deactivation may also result.[30] Routine catalyst cleaning is recommended every 3–12 months,[31] and typically catalysts have a 2 to 5 year lifetime in standard use.[32]

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[26] Crocker, et al., op. cit.
[27] Laznow, et al., op. cit.
[28] Laznow, et al., ibid.
[29] Crocker, et al., op. cit.
[30] Chen, et al., op. cit.
[31] Tyler, op. cit.
[32] Schnelle, Jr., K.B., Brown, C.A., *Air Pollution Control Technology Handbook*, Chapter 13, CRC Press, Boca Raton, FL, 2002.

In a catalytic version of a regenerative thermal oxidizer (a thin layer of catalyst atop the ceramic bed to be heated by the effluent gas) at an oriented strand board manufacturing plant, a VOC-laden gas containing particulates consisting of carbonates, fatty acid salts and sulfates was treated, after particulates removal using an electrostatic precipitator. Process upsets created particulate masking of the catalyst surface reducing VOC DREs from ~85–95% to ~70–75% before the catalyst was washed.[33]

Adsorption

Adsorption units are typically packed beds filled with a carbon adsorbent through which the VOC-laden gas flows. Although adsorption capacity drops as gas concentration decreases,[34] desorption units can be designed to most efficiencies, and is useful for VOC removal down to less than 1 ppmv outlet concentrations.[35]To ensure VOC breakthrough from the bed does not occur, outlet bed concentrations are usually continuously monitored. Feed streams must be cooler than 50–60°C and less than 50% relative humidity to avoid substantial reduction in adsorptive capacity. As heats of adsorption are typically about twice the heat of vaporization for VOCs, high organic concentrations (>10,000 ppm) can lead to overheating of adsorption beds and bed fires if air is present. Halocarbons slowly oxidize in carbon adsorbers, leading to corrosion problems unless acid-resistant materials are used for equipment construction.

Simple and complex metal oxides can also be used as adsorbers for their selectivity and preference for polar compounds. However, moisture renders many metal oxides ineffective since many useful materials like silica gel and molecular sieves are also excellent dessicants. Sorbents may also be impregnated with a chemical reagent, where the reactant converts the pollutant into a harmless or adsorbable material. An example is the impregnation of carbon with bromine to capture ethylene.[36]

Adsorbent wheels are a rotating bed of carbon or zeolite adsorbent that continually collects VO's from air while a portion of the bed is regenerated with hot gas. Successful applications of this technology have achieved 90-95% removal efficiencies. These are typically used to treat high-flow (>10,000 scfm) low-concentration (e.g., <2.5% LFL, <1,000 ppm[37]) streams. While zeolite wheels are less affected by humidity and more resistant to fire damage, highly polar organics like methanol and low boiling compounds like ethane adsorb poorly.

Adsorbers can be single-use, or regenerated using steam or hot air. Regeneration creates either a wastewater or more concentrated gas that requires secondary treatment. Separation of the pollutant from the stripping gas is sometimes difficult, but gas

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[33] Nguyen, P.H., Chen, J.M., *Proceedings of the Air & Waste Management Association's Annual Meeting & Exhibition*, Paper #98-MP22A.07, San Diego, California, June 14–18, 1998.
[34] Laznow, et al., op. cit.
[35] Crocker, et al., op. cit.
[36] Crocker, et al., ibid.
[37] Crocker, et al., ibid.

concentration by adsorption may be desirable if thermal oxidation is the preferred means of VOC destruction.[38]

As a possible indication of actual industrial performance, a Northrop Corp. facility employing a carbon adsorption unit with 99+% test capture efficiency for paint solvents (<100 ppm VOC stream) was issued an air emissions permit requiring only a destruction efficiency of no less than 95%.[39] Stuck or leaking inlet or outlet valves are very common problems thatlead to high exit concentrations and possibly shorter-than-expected adsorption times.[40]

Adsorbers require continuous organic inlet and outlet concentration monitoring to determine when breakthrough is imminent and begin the bed regeneration or replacement process. Gas pre-treatment may be necessary to remove particulates, entrained liquids or high-boiling compounds (if regenerable adsorber) to maintain high adsorbent capacity.[41] Regular carbon adsorbability and contaminant retention testing of adsorber bed samples from various bed locations is recommended to ensure proper bed cycle times, as adsorber particles erode and pores become plugged with contaminants and foreign matter.[42] Ductwork leaks can negatively impact DREs by releasing untreated gas on the pressure-side of the air fan or by reducing the adsorption driving force through diluting the contaminated air stream on the suction-side of the fan.[43]

<u>Biofiltration</u>

Biofiltration is a new but fully industrial method often used for odor control and reduction of dilute VOC emissions (lowest investment for certain VOCs at <500 ppm). VOC-laden air is passed through beds of immobilized microorganisms with typical residence times of 0.5 to a few minutes, to achieve VOC reductions of 80–95%. This process has difficulty with low aqueous solubility compounds and those that resist oxidation, such as methylene chloride. Biofiltration may also be unsuitable in cases where the gas contains significant quantities of components that are toxic to microorganisms (e.g., SO_2).[44] Uneven gas distribution is the primary difficulty in scaleup to very large scale, where gas channeling, bed dry spots, and sometimes anaerobic oxidation reduce destruction efficiency and possibly generate odors. Similar biological oxidation devices are bioscrubbers where oxidation is conducted in a vessel separate from absorption, and biotrickling filters where water flows continuously through the substrate.

In addition to the expected maintenance of moisture, nutrient levels, pH and low bed pressure drops to maintain the microbial population, periodic “fluffing” of the filter material through addition of fresh components is required to combat settling and

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[38] Crocker, et al., ibid.
[39] Zerbonia, et al., op. cit.
[40] Kovach, J.L., “Gas-Phase Adsorption,” *Handbook of Separation Techniques for Chemical Engineers*, 2nd ed. (P.A. Schweitzer, editor), McGraw-Hill Book Co., San Francisco, 1988.
[41] Mycock, J.C., McKenna, J.D., Theodore, L., *Handbook of Air Pollution Control Engineering and Technology*, Chapter 10, Lewis Publishers, New York, 1995.
[42] Mycock, et al., Chapter 10, ibid.
[43] Mycock, et al., Chapter 10, ibid.
[44] Leson, G., Winer, A.M., *J. Air Waste Manage. Assoc*., 41 (8), pp. 1045–54, 1991.

compaction problems that arise naturally as the biofilter bed materials are consumed or degraded to yield smaller particle sizes[45]. Also, clumping of fine filter particles can lead to filter material crack formation, resulting in gas channeling.[46] Periodic discharge of filter-bed excess water typically containing dissolved off-gas pollutant compounds is usually required to avoid solids buildup in the gas humidifier, to where such water is usually recycled to minimize wastewater production.[47]In some cases, gas pre-treatment may be required to reduce high particulate loads to minimize clogging in the air distribution and/or humidification systems as well as filter material.[48]

Eastman Kodak Company's 1996 monitoring of a newly installed 20,000-cfm (566 m^3/min) biofilter treating VOC offgases from batch chemical manufacturing encountered the following problems during the first year of facility startup and operation[49]: (1) inability to reach the designed and permit-required 90% DRE (average actual DRE 84% with 44% standard deviation) after the actual average feed VOC concentration was of order 50% below the 130 ppmv design VOC concentration 90% of the time, (2) a 58% average and highly variable DRE after the first 21 days of operation where negative removal efficiencies likely caused by release of captured VOC into low concentration air were observed after large inlet concentration "spikes", (3) large negative removal efficiencies for the first several hours before reaching a 6-day average 76% DRE during startup after a 125 hr scheduled shutdown, (4) 15% lower heptane DRE during a ~10 day biofilter acclimation period, and (5) destruction efficiencies drop as offgas VOC concentrations decrease. A Bio-Reaction Industries Inc. biofilter attached to paint mixing vats experienced a reduced removal efficiency (63% actual versus 75% design) when 3000 ppmv feed VOC concentrations far exceeded the 300–1,200 ppmv scrubber design estimate.[50]

<u>Condensation</u>

Condensation is a process where high pressure and/or cooling is typically utilized to induce near-saturated VOC-laden gases to form liquid droplets for collection. Pollutants with low ambient vapor pressures may also be effectively controlled using condensation.[51] Condensation is usually exploited industrially for gas flows <2,000 scfm, condensable VOC concentrations >5 000 ppm, and required DREs <90%.[52] Surface condensers involve direct contact of the air stream to a cold surface, while contact condensers spray a cool liquid into the gas stream. Contact condensers can be very economical, but often simply transfer an air treatment problem into a waste liquid treatment or emission[53] problem. Surface condensers cooled by 5°C chilled water can

45 Michelsen, R.F., "Biofiltration," *Handbook of Air Pollution Control Engineering and Technology* (Mycock, J.C., McKenna, J.D., Theodore, L., editors), Chapter 21, Lewis Publishers, New York, 1995.
46 Michelsen, ibid.
47 Leson, G., et al., op. cit.
48 Leson, et al., ibid.
49 Gilmore, G.L., Briggs, T.G., *Proceedings of the Air & Waste Management Association's Annual Meeting & Exhibition*, Paper #97-RA71C.02, Toronto, Canada, June 8–13, 1997.
50 Stewart, W.C., Ashlock-Barton, T., Thom, R.R., *Environmental Progress*, 20 (4), pp. 207–11, 2001.
51 Crocker, et al., op. cit.
52 Laznow, et al., op. cit.
53 Laznow, et al., ibid.

achieve 50–90% recovery for VOCs in saturated air or nitrogen under summer conditions, 90–95% recovery using -30°C refrigerated systems, and 99% collection for gasoline, vinyl chloride and methylene chloride when boiling nitrogen condensers (-185°C) are employed. Because of the cost of using refrigerated or cryogenic systems, condensation is rarely used alone, particularly when outlet concentrations must be below a few ppmv.[54]If the process gas must be cooled more than ~40–50°C from its initial temperature to attain required condensibles removal, a fog of <1µm particles can form that can be particularly difficult to collect, a problem more usually seen in surface condensers.[55]

Fouling of heat exchanger surfaces is the typical condenser operation problem that is usually detected by increasing pressure drop and decreasing condenser performance. If severe, some heat exchanger tubes may become completely plugged, causing thermal stresses and physical equipment damage.[56] Depending on the nature of the deposited material, foul can be removed by rinsing, elevated temperatures, chemical cleaning, or mechanical methods.[57]

Membrane Separation

In a typical membrane recovery system, ambient temperature VOC-laden gas is compressed, passed through a condenser operating above the freezing point of water, and then sent to modulesof membranes where organic solvents preferentially permeate through the membrane. Single stage units often achieve 50–98% recoveries. Despite the high compression costs, membranes are sometimes used in place of adsorption, particularly when collecting halogenated compounds. Most membrane separation systems are used for <200 scfm air streams.

Absorption

In absorption, VOCs are captured from the gas into a relatively non-volatile liquid phase. Absorption units can be designed for many efficiencies, and are typically used for gas streams of appreciable volatile organic concentrations or dilute streams containing contaminants with high solvent solubility.[58] Absorbers can come in many forms such as packed beds, plate towers, spray towers, and venturi scrubbers. Common absorbing liquids used are high boiling hydrocarbons (recent laboratory studies show vegetable oil has >90% capture efficiencies[59]), water, caustic solutions, and amines Absorption produces wastewater or a waste liquid that must often be treated before discharge or recycle, such as through the use of a gas stripper.

Acid gases such as HCl, HF, and SiF_4 can be absorbed in water, especially if the water has alkaline pH. Similarly, alkaline gases (like ammonia) can be treated with acid waters like dilute sulfuric, phosphoric or nitric acids. Single-pass scrubbing solutions like these

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[54] Crocker, et al., op. cit.
[55] Crocker, et al., ibid.
[56] Hounsell, G., "Condensers," *Handbook of Air Pollution Control Engineering and Technology* (Mycock, J.C., McKenna, J.D., Theodore, L., editors), Chapter 12, Lewis Publishers, New York, 1995.
[57] Hounsell, ibid.
[58] Crocker, et al., ibid.
[59] Johnson, J., Parker, W., Kennedy, K., *Environmental Progress*, 19 (3), pp. 157–66, 2000.

can be used as fertilizer ingredients.[60] Pollutants with limited solvent solubility usually require impractically large quantities of solvent to achieve required capture efficiencies. However, rare cases like the use of alkaline tidal water to capture SO_2 at the Battersea and Bankside electric power stations do exist.[61]

Absorbers require fairly regular operational checks and maintenance to ensure operation within the design parameters. Abnormal readings encountered in daily logs of system pressures, temperatures, flows and other parameters require serious investigation to prevent one of a series of potential problems negatively impacting performance such as: (1) unexpected changes in flow rates or other absorber operating parameters due to human error or other causes, (2) obstruction or leaking in liquid distributor/spray nozzles or piping, (3) degradation or settling of bed packing (if applicable), (4) loss of chemical feed in the case of reactive absorbers, and (5) plugging or channeling in the liquid anti-entrainment device.[62] After approximately two weeks after startup or major process/operation changes, the absorber should be shutdown to allow for addition of bed packing after settling (in packed beds) and for checks for nozzle plugging which often occur during this time period.[63] Although in terms of capacity absorbers are generally overdesigned and the typical lower flow rates through the system generally increase absorption efficiency, too low gas input can cause channeling to hurt absorber and anti-entrainment device performance; also a column running dry could in some cases cause heavy formation of solids, crystals or other matter that will negatively impact gas liquid contacting.[64]

Liquid and/or Solid Particulate Scrubbing in Brief

In air pollution control, particulates in the gas stream may be either a liquid or solid, or a combination of the two.[65] As a result, solid and liquid particulate removal from a gas stream are often considered together. In many general scrubber technical references, significant discussion of the theories for the design of each of several particulate scrubbers can be found. However,

> "… the difficulty of theoretical treatment of dust-collection phenomena has made necessary simplifying assumptions, with the introduction of corresponding uncertainties. Theoretical studies have been hampered by a lack of adequate experimental techniques for verification of predictions. Although theoretical treatment of collector performance has been greatly expanded in the period since 1960, few of the resulting performance models have received adequate experimental confirmation because of experimental limitations….The design of industrial-scale collectors still

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[60] Crocker, et al., op. cit.
[61] Crocker, et al., ibid.
[62] Mycock, et al., Chapter 9, op. cit.
[63] Mycock, et al., Chapter 9, ibid.
[64] Mycock, et al., Chapter 9, ibid.
[65] Crocker, et al., op. cit.

> rests essentially on empirical or semiempirical methods, although it is increasingly guided by concepts derived from theory. Existing theoretical models frequently embody constants that must be evaluated by experiment and that may actually compensate for deficiencies in the models."[66]

Hence, the performance of a given particulates scrubber is likely dependent on the skill and experience of the equipment designer, and could potentially vary significantly between individual designers or design teams. A designer's knowledge of the process to be controlled is generally expected to largely determine the industrial success of the proposed design.

Figure 3 shows some of the industrially accepted values for solid and/or liquid scrubbing efficiency in several types of equipment as a function of particle size. Table 3 also provides another source of accepted values illustrating the wide variance in performance vs. particle size, and hints towards some of the other factors to consider in particle scrubbing equipment operation and performance. Hence, particulate scrubbing efficiencies are likely very process-dependent, with maintenance of high removal efficiencies very related to sustaining consistent feed particle sizes. Particulate scrubbers can require significant preventive maintenance[67] and can encounter problems that can impact collection efficiency significantly. For example, baghouses can encounter dirty stack discharge resulting from bag failure or leakage, faulty bag clamps, seal failure at clean/dirty air connection joints, insufficient filter cake, and overly porous filter bags.[68] Electrostatic precipitators often do not respond well to changes in process gas temperature, gas pressure, flow rate, gaseous or chemical composition, dust loading, particulate size distribution, or electrical conductivity of the dust.[69]

Although very difficult to find in the published technical literature, experience in the field does suggest that equipment designed particulate collection efficiencies can vary significantly from actual operating performance. Cora and Hung mention that although baghouses are designed for 99–99.9% particulate collection/removal efficiencies, actual operating removal efficiencies may differ slightly, down to the level of 95%.[70]

Despite solid and liquid particulate emissions not being of primary interest here, volatile organic compound emissions may result from the release of uncaptured particulates. Organic odor compounds represent an important industrial example, originating as a gas or particulates.[71] VOC emissions from particulates could theoretically come from desorption from emitted solid particulate surfaces (such as when particulates are released into a warmer ambient environment) and from evaporation of or from uncaptured liquid droplets (such as when emitted into a drier and/or warmer ambient environment).

[66] Pell, M., Dunson, J.B., "Gas-Solid Operations Equipment," *Perry's Chemical Engineer's Handbook*, 7th ed. (Perry, R.H., Green, D.W., Maloney, J.O., ed.), pp. 17–26, McGraw-Hill Co., Inc., New York, 1997.
[67] Mody, V., Jakhete, R., *Dust Control Handbook* (reprint ed.), Noyes Publications, Westwood, NJ, 1988.
[68] Mody, et al., ibid.
[69] Mody, et al., ibid.
[70] Cora, M.G., Hung, Y.T., *Environmental Quality Management*, 11 (4), pp. 53–64, 2002.
[71] Crocker, et al., op. cit.

Conclusions

From this relatively broad survey of actual industrial VOC gas scrubber capabilities, a few select citations garnered from a large number of related literature search hits suggest significant differences between actual and design performance in some technologies (recuperative and regenerative thermal oxidizers, catalytic oxidizers, adsorption), although a portrayal of the entire gas scrubbing industry was elusive. Lack of scrubber system maintenance can contribute to even larger variances. Although scrubber capabilities are continually being improved, "typical" industrial single-pass performance of VOC gas scrubbers generally ranged from ~80 to 99% as of the early-to-mid 1990s, except in the unusual cases where lower-efficiency condensers are used. Industrial odor control experience suggests that the imperfect solid and/or liquid particulates capture (possibly as low as 95% despite design for 99+% capture efficiency) can also lead to VOC releases. Changing the VOC composition in the gas stream without modifying scrubber equipment or operating conditions could also lead to significant deterioration in attainable DREs (e.g., adding halocarbons to a hydrocarbon-air stream fed to a thermal oxidizer). Biofilters appear to encounter performance problems during initial startup, during startup after prolonged scheduled shutdowns, and addition of new compounds to the off-gas.

Future Work/Improvements

The low incidence of quantitative industrial VOC gas scrubber performance data encountered in this literature survey strongly suggests that such information is closely guarded, likely for proprietary reasons and possibly for political reasons as well (e.g., avoid providing unflattering information). However, further possible literature-related searches include: (1) examination of state and federal EPA reports on regulatory emissions violators, (2) full exploration of US and foreign patents for possible industry experiential information, (3) time to gather and evaluate data in excluded US government agency reports available through Office of Scientific and Technical Information. Non-literature sources, such as interviews of industrial and/or academic consultants who have each individually served both industrial and regulatory clients, could be very valuable.

Acknowledgments

The author would like to thank Dr. August T. Droege for providing the motivation for and help with an early literature search in this study, and David R. Parks for some early advice regarding possible literature search directions.

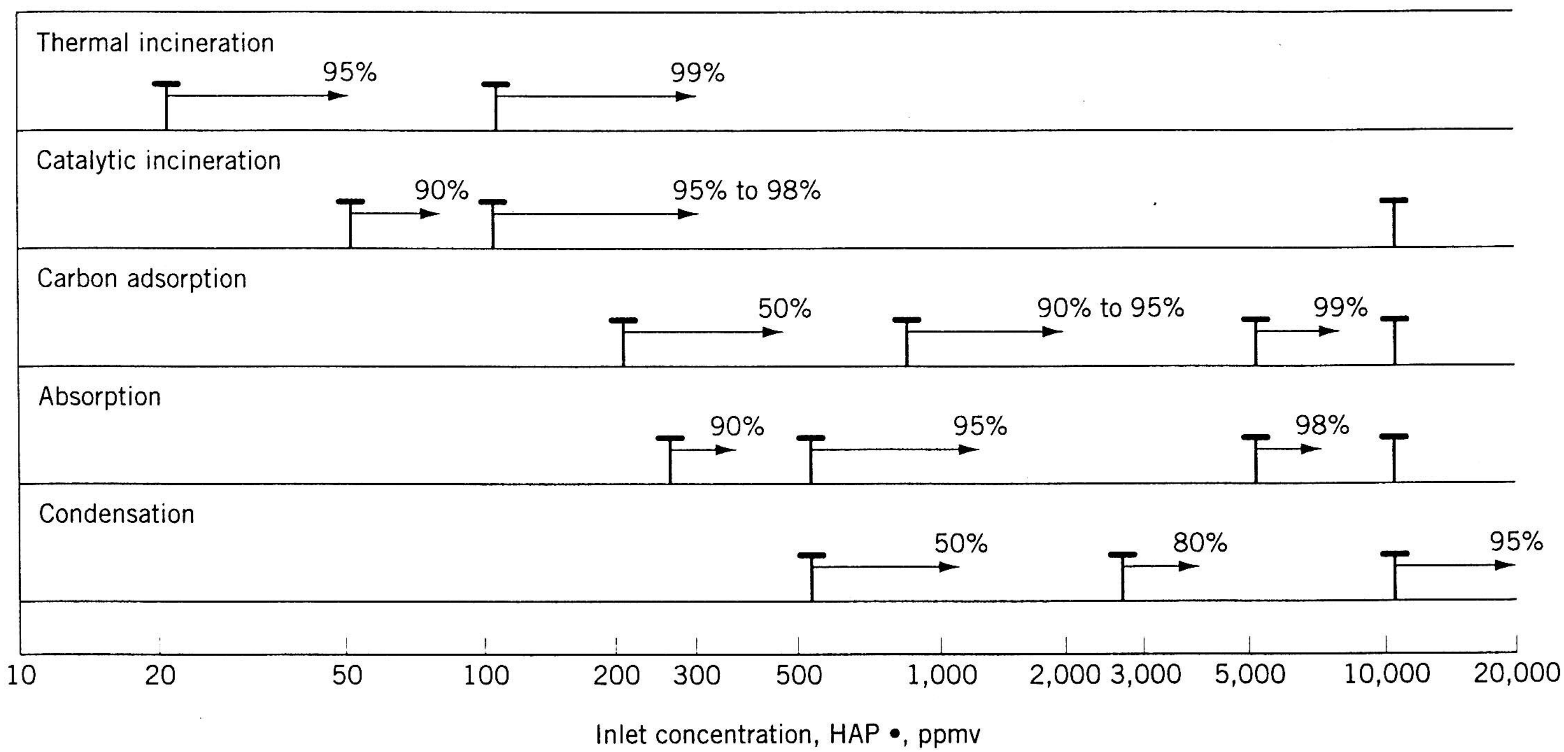

Figure 1. USEPA's 1991 Expected Approximate Percent Reductions for Volatile Organic Compound Treatment [from Ref. 12]

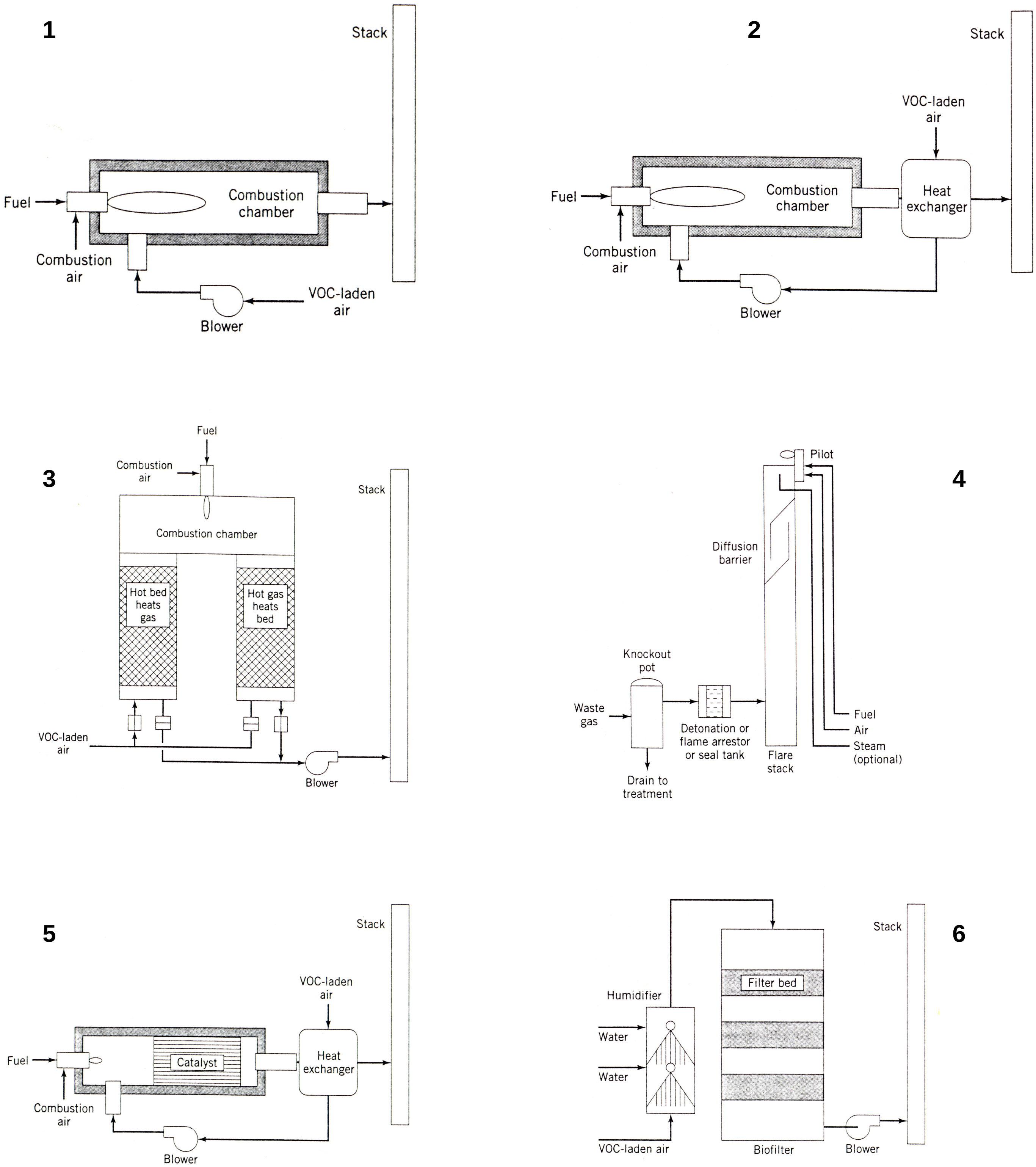

Figure 2. Schematics of various volatile organic compound air pollution techniques: (1) Afterburner, (2) Recuperative thermal oxidizer, (3) Regenerative thermal oxidizer, (4) Flare, (5) Catalytic Oxidizer, (6) Biofilter [from Ref. 10]

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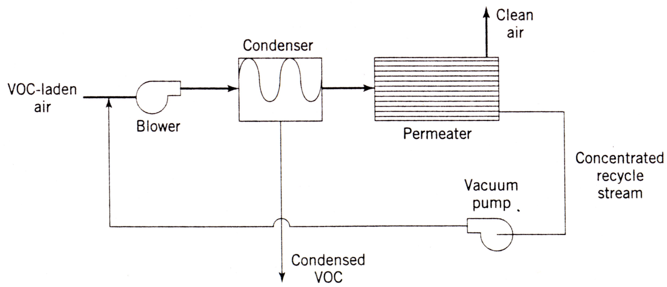

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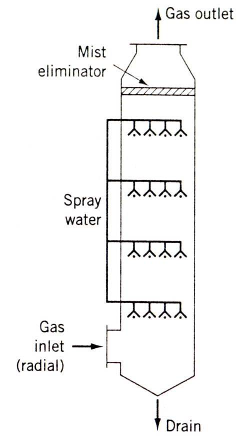

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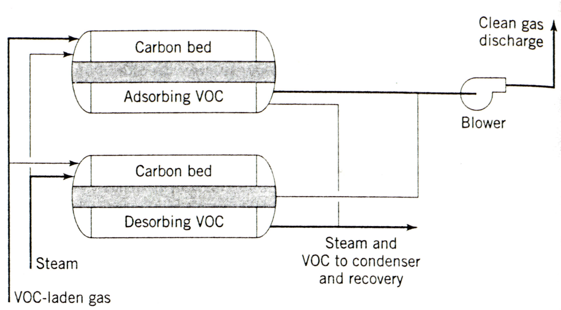

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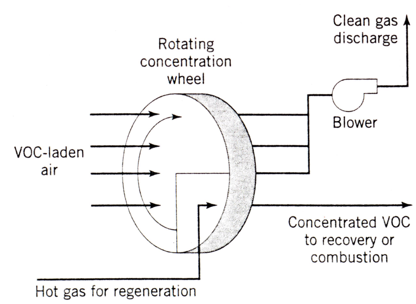

Figure 2. (continued) Schematics of various volatile organic compound air pollution techniques: (7) Membrane technology, (8) Spray absorber, (9) Adsorber, (10) Adsorbent (concentration) wheel [from Ref. 10]

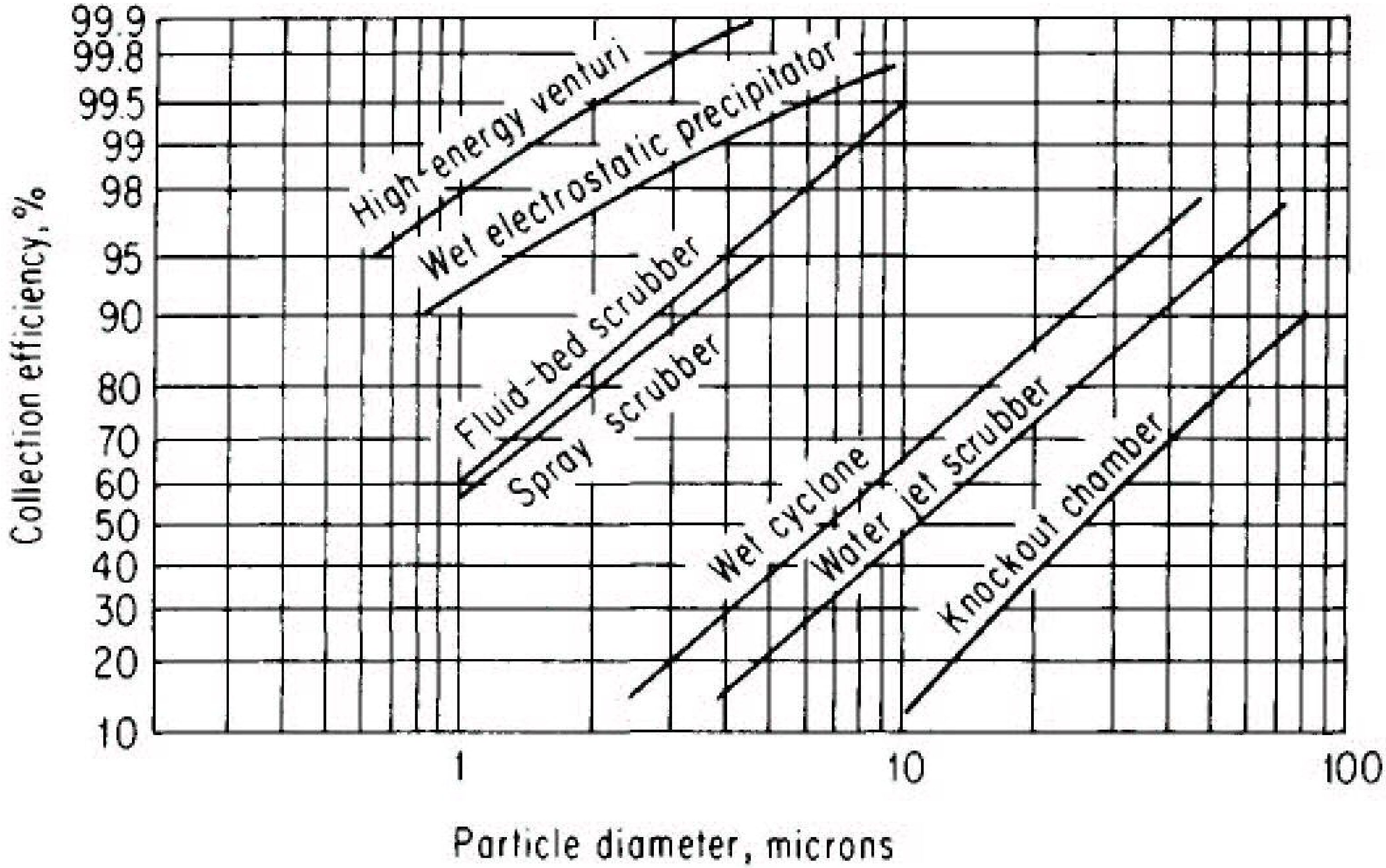

Figure 3. Solid and/or Liquid Particle Scrubber Performance Affected by Particle Size [from Ref. 3]

Table 4. Key Emission Stream and HAP Characteristics for Selecting Control Technologies for Organic Vapors from Point Sources

	Emission Stream Characteristics					HAP Characteristics[a]			
Control Device	HAP/Organics Contents[b], ppmv	Heat Content, BTU/scf	Moisture Content, %	Flow Rate scfm	Temp, °C	Molecular Weight, lb/lb · mole^{-1}	Solubility	Vapor Pressure, mm Hg	Adsorptive Properties
Thermal incinerator	>20; (<25% of LEL[c])			<50,000[d]					
Catalytic incinerator	50–10,000; (<25% of LEL[c])			<50,000					
Flare		>300[e]		<2,000,000[f]					
Boiler/process heater[g]		>150[h]		Steady					
Carbon adsorber	700–10,000 (<25% of LEL[c])		<50%[i]	300–200,000	≤54	45–130			Must be able to absorb on/desorb from available adsorbents
Absorber	250–10,000			1,000–100,000			Must be readily soluble in water or other solvents		
Condenser	>5,000–10,000			<2,000				>10 (at room temp)	

[a] Refers to the characteristics of the individual HAP if a single HAP is present and to that of the HAP mixture if a mixture of HAPs is present.
[b] Determined from HAP/hydrocarbon content.
[c] For emission streams that are mixtures of air and VOC; in some cases, the LEL can be increased to 40 to 50% with proper monitoring and control.
[d] For packaged units; multiple-package or custom-made units can handle larger flows.
[e] Based on the EPA's guidelines for 98% destruction efficiency.
[f] Units: lb/h. Source: Ref. 12.
[g] Applicable if such a unit is already available on-site.
[h] Total heat content.
[i] Relative humidity. Applicable for HAP concentration less than about 1000 ppmv.

Table 1. USEPA's 1991 Guidelines for Volatile Organic Compound Control Technology Selection [from Ref. 12]

VOC Control Technology	Typical Application Flow Rate[a]	Secondary Environmental Impacts
Absorption	Very broad range	Sometimes wastewater
Biofiltration	Very broad range with units above 150,000 cfm	Spent substrate (normally infrequent) Possibly condensate and drainage
Catalytic oxidation	Typically 1,000 to 15,000 cfm Units above 50,000 cfm, especially when oxygen content of gas is low	CO_2, NO_X, CO (normally minor) Sometimes acids (when wastes contain halogens, etc.) Spent catalyst (normally infrequent)
Condensation	Typically under 1,000 cfm, most under 100 cfm	Sometimes wastewater Possibly RCRA hazardous waste
Flare	Very broad range, typically under 200 cfm if most fuel is supplemental	Air emissions—normally minor Light and heat
Membrane technology	Most under 200 cfm	Wastewater Spent permeate modules (infrequent)
Regenerated adsorption	Most over 1,000 cfm	Wastewater Spent adsorbent (normally infrequent)
Single-use carbon adsorption	Most under 1,000 cfm	Spent adsorbent (sometimes substantial and often a RCRA hazardous waste)
Thermal oxidation		
Afterburner	Under 3,000 cfm	CO_2, NO_X, CO (normally minor) Sometimes acids (when wastes contain halogens, etc.)
Recuperative thermal oxidizer	1,000–15,000 cfm	
Regenerative thermal oxidizer	5,000 to very large, >200,000 cfm	
Concentration wheel with thermal oxidizer	10,000 cfm to very large	

[a]1 cfm = 1.7 m^3/h

Table 2. Typical Gas Stream Flow Rates for Secondary Environmental Impacts of VOC Control Technology Applications [from Ref. 10]

TABLE 4 Equipment Selection Chart

Collector	Applicable Particle Size Range (μm)	Pressure Drop (in. w.c.)	Degree of Cleaning to Be Expected	Maximum Acceptable Temperature (°C)	Condition of Effluent	Dew Point Sensitivity	Effect of Particle Density
Settling chambers	>150	<1	50% on particles below 50 μm and approximately 95% on particles above 300 μm	500	Dry or wet by use of conditioner	Not too sensitive	Efficiency increases with density
Cyclones	>10	1–3	80% on particles below 20 μm and greater than 95% on particles above 50 μm	500	Dry or wet by use of conditioner	Critical	Efficiency increases with density
Spray towers	>3	2–7	98% on particles above 5 μm and 50% on particles below 3 μm	200–250	Wet	Not sensitive; may influence material of construction	Little effect unless cyclone principle also embodied
Venturi scrubbers	>0.3–1.0	15–30	90–99% on particles below 5 μm	200–250	Wet	Not sensitive; may influence material of construction	Little effect on efficiency
Bag filters	>0.5–1.0	1–10	95–99% on particles below 5 μm	200–250	Dry or wet by use of conditioner	Very critical	No effect on efficiency
Electrostatic precipitators	>0.001	0.25–0.5	80% to over 99% on all particles	500	Dry or wet by use of conditioner	Critical except for irrigated precipitator	Little effect on efficiency
High-efficiency paper filters	>0.3–0.5	0.5–2.0	Up to 99.9% on all particles below 5 μm	50	Dry	Very critical	No effect on efficiency

Table 3. Solid and/or Liquid Particle Scrubber Equipment Selection Chart [from Ref. 9]